

Surface modes on a polymer gel of finite thickness

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(Received 23 September 1992; accepted 30 October 1992)

The fluctuations in the height of the free surface of a polymer gel of finite thickness are analyzed in the limit where the period of elastic oscillations is small compared to the viscous relaxation time. In this limit, the dominant forces in the momentum conservation equation are the elastic and surface tension forces; the viscous forces enter as a subdominant correction. Zero stress boundary conditions are applied at the free surface, while two different types of boundary conditions are considered at the other surface— for “grafted” gels zero displacement conditions are applied, while for “adsorbed” gels the displacement normal to the surface is zero but the surface is permitted to move in the lateral direction. There are multiple frequencies of oscillation, all of which are consistent with the boundary conditions, and it is found that the frequency and the decay rates of the oscillations are lower for the adsorbed gels. The static structure factor is calculated from the energy storage due to the elastic strain, surface deformation, and kinetic energy of motion. The structure factor has a peak at a nonzero value of the wave number for a grafted gel, while the maximum occurs at zero wave number for an adsorbed gel. An increase in the surface tension reduces the magnitude of the peak, and shifts it to lower values of the wave number.

I. INTRODUCTION

The surface properties of grafted polymers and gels are important in many applications. Surface oscillations provide a mechanism for energy dissipation in polymer tribology applications. In biological systems, fluids are transported through tubes with compliant walls that are made of gels, and oscillations of the walls are thought to be responsible for increasing the drag force in these tubes.¹ Although the bulk properties of polymers have been extensively studied,^{2,3} the surface properties have received less attention. However, recent advances in experimental methods such as surface light scattering techniques have made it possible to probe the surface modes of polymer gels.⁴

The majority of the previous theoretical analyses have used single fluid models to analyze the surface modes. In this approach, the polymer is treated as a viscoelastic fluid described by the non-Newtonian Navier–Stokes equations, in which the shear stress is a nonlinear function of the strain rate.^{5–7} A different approach was used by Harden, Pleiner, and Pincus⁸ to calculate the surface modes on an infinite gel. They wrote coupled equations for the fluid velocity field and the displacement field of the polymer network. In addition to the shear stress due to the fluid flow, their description included an elastic stress due to the straining of the polymer network. This additional stress gives rise to features not present in classical fluids, where only the viscous and surface tension forces are present. In addition, this elastic term can give rise to surface instabilities even in the absence of inertia,⁹ whereas the surface instabilities of viscoelastic fluids are inertial in nature.⁶

In this paper we analyze the surface modes on polymer gels of finite thickness, and we find that these can be significantly different from the modes on semi-infinite gels analyzed by Harden *et al.*⁸ Zero stress boundary condi-

tions are appropriate at the free surface of the gel, while two types of boundary conditions are applied at the other surface: for “grafted gels” which are fixed to a flat surface, zero displacement conditions are applied at this surface; while for “adsorbed gels” which are bounded by a flat surface, the displacement in the direction normal to the surface is zero, but the surface is permitted to move freely in the tangential direction and zero shear stress conditions are applied at this surface. We find that there are multiple resonant frequencies at a given wave number, all of which are consistent with the boundary conditions imposed at the two surfaces. In addition, the surface modes in the capillary regime, in which the surface tension forces are large compared to the viscous and elastic forces, are qualitatively different for finite gels. In this limit, there exist nontrivial solutions for the frequency spectrum of finite gels which are not permissible in gels of infinite extent. Another interesting observation is that the frequency and decay rate of the surface modes for grafted gels are very different from those for adsorbed gels.

There are two important time scales in the problem—the elastic oscillation time for the strain field of the polymer network, and the viscous relaxation time for the fluid velocity field. Here we analyze the limit where the elastic time is small compared to the viscous relaxation time. A scaling analysis in Sec. II indicates that this assumption is valid when the gel thickness is large compared to about 1 μm for typical values of gel elasticity and fluid viscosity. In this limit, there is a balance between the elastic and surface tension forces at leading order. Since both these forces are conservative, the surface modes propagate undamped over time intervals comparable to the elastic time; the viscous damping becomes significant over much larger intervals comparable to the viscous relaxation time. The high fre-

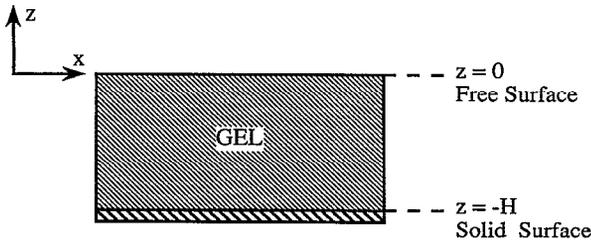


FIG. 1. Gel configuration and coordinate system used in the analysis.

quency elastic oscillations could have a significant effect in applications where there is fluid flow past a polymer gel, since the oscillations change the nature of the flow at the surface of the gel.

The separation of time scales facilitates an asymptotic approach in which there is a balance between the elastic and surface tension forces at leading order, and the viscous terms enter as a first order correction. The mass and momentum conservation equations are derived in Sec. II and the dispersion relation is calculated from the linearized equations of motion in Sec. III. The surface mode structure factor is calculated from the energy storage spectrum in Sec. IV. We end with a brief discussion of the important results in Sec. V.

II. EQUATIONS OF MOTION

The system, shown in Fig. 1 consists of a gel of finite thickness H and infinite lateral extent occupying the region $H < z < h(x)$, where $h(x)$, the equation of the surface of the gel, is equal to zero in the unperturbed state. The $z > h(x)$ space is occupied by vapor, and zero stress boundary conditions are applied at the surface $h(x)$. The boundary conditions at the surface, at $z = -H$ will be discussed shortly. The polymer network is modeled as an elastic medium of density ρ_p , shear modulus E , and compressional modulus K , and the fluid is an incompressible Newtonian fluid with viscosity η and density ρ_f . We first derive the momentum conservation equations for the network and the solvent, and return later to the appropriate form of the mass conservation condition.

The momentum conservation equations for the fluid velocity and polymer displacement field are

$$\rho_f \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = \nabla \cdot \boldsymbol{\sigma}^f + f_I(\mathbf{u}, \mathbf{v}), \quad (1)$$

$$\rho_p \left(\frac{\partial^2 \mathbf{u}}{\partial t^2} \right) = \nabla \cdot \boldsymbol{\sigma}^p - f_I(\mathbf{u}, \mathbf{v}). \quad (2)$$

Here, $\boldsymbol{\sigma}^p$ and $\boldsymbol{\sigma}^f$, the polymer and fluid stress tensors, are of the usual form:^{10,11}

$$\sigma_{ij}^p = E \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \left(K - \frac{2}{3} E \right) \delta_{ij} \left(\frac{\partial u_l}{\partial x_l} \right), \quad (3)$$

$$\sigma_{ij}^f = -p \delta_{ij} + \eta \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) - \frac{2}{3} \eta \left(\frac{\partial v_l}{\partial x_l} \right). \quad (4)$$

The interaction force per unit volume between the solvent and the polymer, $f_I(\mathbf{u}, \mathbf{v})$, is treated as a local frictional force that is proportional to the difference in the local polymer and solvent velocities:

$$f_I(\mathbf{u}, \mathbf{v}) = \chi \left(\frac{\partial \mathbf{u}}{\partial t} - \mathbf{v} \right). \quad (5)$$

The form of the proportionality constant χ has been discussed previously in literature,^{8,12} and there is general agreement that it scales as η/ξ^2 , where ξ is the characteristic mesh size of the polymer network. This can be shown by a simple scaling argument.⁸ The polymer network may be viewed as a collection of close packed capillaries of cross section $(1/\xi^2)$, and the resistance of each capillary to the solvent flow scales as (η/ξ^4) . Thus the resistance of the network per unit area, which is the friction constant χ , scales as (η/ξ^2) .

The mesh size in polymer gels is $O(100 \text{ \AA})$ or less, and is much smaller than any macroscopic length scale of interest in the problem. In the bulk of the gel, the divergence of the polymer and fluid stresses scale as $(\eta v/H^2)$ and (Eu/H^2) , where v and u are the orders of magnitude of the velocity and displacement fields while the frictional force per unit area scales as $(\eta \Delta v/\xi^2)$, where Δv is the difference in the polymer and fluid velocities. Therefore, the force balance condition in the gel requires the difference in the fluid and network velocities to be $O(\xi/H)^2$ smaller than the velocity of the gel, and at leading order we can assume that the polymer and fluid velocities are equal:

$$\frac{\partial \mathbf{u}}{\partial t} = \mathbf{v}. \quad (6)$$

The limit in which this condition is valid is called the "infinite coupling limit," which was studied by Harden *et al.*⁸ Following Harden, we make the infinite coupling approximation in this paper. In this limit, the equations of motion reduce to

$$\rho \left(\frac{\partial^2 \mathbf{u}}{\partial t^2} \right) = -\nabla p + E \nabla^2 \mathbf{u} + \eta \nabla^2 \left(\frac{\partial \mathbf{u}}{\partial t} \right), \quad (7)$$

where ρ is the sum of the densities of the polymer and the fluid ($\rho_p + \rho_f$). In the infinite coupling limit, the mass conservation equation has the same form as that for an incompressible medium:

$$\nabla \cdot \mathbf{u} = 0. \quad (8)$$

At the surface of the gel at $z = h(x)$, we require the total normal and shear stresses to be zero:

$$\text{At } z = h(x): \quad \sigma_{zz} = \gamma \nabla_t^2 h(x), \quad \sigma_{xz} = 0. \quad (9)$$

Here, σ_{zz} and σ_{xz} are the sum of the stresses in the fluid and the polymer, γ is the surface tension, and ∇_t^2 is the transverse Laplacian operator. As mentioned in the Introduction, we distinguish between two types of gels based on the boundary conditions at the surface $z = -H$: gels which are fixed to a rigid surface, referred to as "grafted gels;" and gels which are bounded normal to the surface but free to move in the tangential direction, which are termed "adsorbed gels."

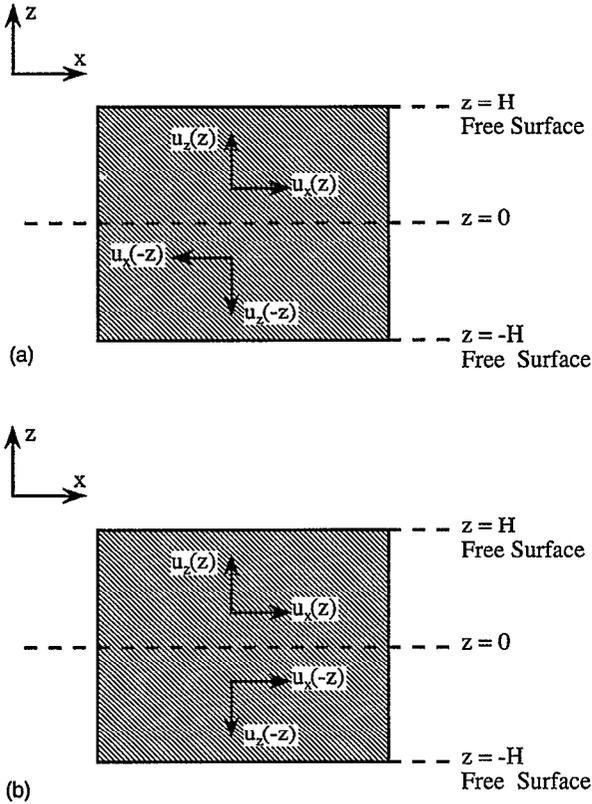


FIG. 2. Antisymmetric (a) and symmetric (b) modes of oscillation of a finite gel subjected to zero stress conditions at both surfaces.

For *grafted gels*, we apply zero displacement conditions:

$$\text{At } z = -H: u_z = 0, \quad u_x = 0. \quad (10)$$

The above boundary conditions are also valid at the midplane of a gel of thickness $2H$ which has two free surfaces, and whose oscillations are antisymmetric about the midplane [$u_z(z) = -u_z(-z)$ and $u_x(z) = -u_x(-z)$] as shown in Fig. 2(a).

For *adsorbed gels*, the following boundary conditions are appropriate:

$$\text{At } z = -H: u_z = 0, \quad \frac{\partial u_x}{\partial z} = 0. \quad (11)$$

The above boundary conditions are also appropriate at the midplane of a gel of thickness $2H$ with two free surfaces, whose surface oscillations are symmetric about the midplane [$u_z(z) = u_z(-z)$ and $u_x(z) = u_x(-z)$] as shown in Fig. 2(b). Since any perturbation can be expressed as the sum of a symmetric and an antisymmetric component, the boundary conditions studied here can be used to analyze all perturbations in a gel of finite thickness with zero stress boundary conditions at both surfaces.

At this point, it is useful to determine the regimes where the viscous, elastic, and surface tension effects dominate. The dimensionless number $[\gamma/(HE)]$ is a measure of the ratio of the surface tension and elastic forces in the gel. For typical values of $E = 10^3 \text{ N/m}^2$ and $\gamma = 20 \times 10^{-3} \text{ N/m}$, the surface tension forces are large compared to the

elastic forces in the gel for $H \gg 20 \mu\text{m}$. The ratio of the elastic and viscous forces is given by the dimensionless number $\epsilon \equiv [\eta^2/(\rho EH^2)]^{1/2}$. For a typical value of $\eta = 10^{-3} \text{ Ns/m}^2$, the elastic forces are large compared to the viscous forces and $\epsilon \ll 1$ for $H \gg 1 \mu\text{m}$. In this limit the elastic and surface tension forces balance each other at leading order, and the viscous forces can be treated as a subdominant correction in an asymptotic scheme in small ϵ . We should also point out that the gravitational force has been neglected in the momentum equations. The ratio of the gravitational and elastic forces is given by the dimensionless number $(\rho g H/E)$, where g is the acceleration due to gravity. It can easily be verified that for the typical values of the density and elasticity listed above, the gravitational forces are important only for $H \sim 0.1 \text{ m}$, and therefore we can neglect gravity for gels with thickness between $1 \mu\text{m}$ and 1 mm , which are considered here.

We nondimensionalize the length scales in the conservation equations (7) and (8) by the thickness of the gel H and time scales by the elastic time $(\rho H^2/E)^{1/2}$. The resulting equations are

$$\nabla \cdot \mathbf{u} = 0, \quad (12)$$

$$\frac{\partial^2 \mathbf{u}}{\partial t^2} = -\nabla p + \left(1 + \epsilon \frac{\partial}{\partial t}\right) \nabla^2 \mathbf{u}, \quad (13)$$

where the pressure p is nondimensionalized by E , and $\epsilon \equiv [\eta^2/(\rho EH^2)]^{1/2}$, is a small parameter. The nondimensional boundary conditions at the free surface are

$$\text{At } z = h(x): \sigma_{zz} = \Gamma \nabla_{\parallel}^2 h(x), \quad \sigma_{xz} = 0, \quad (14)$$

where the stresses are nondimensionalized by E and the dimensionless parameter Γ is $[\gamma/(EH)]$.

III. SURFACE MODE GROWTH RATE AND FREQUENCY SPECTRA

A. Dispersion relations

To determine the frequency spectra, we impose small perturbations on the displacement and velocity field of the form:

$$\mathbf{u}(z, \mathbf{x}, t) = \frac{1}{(2\pi)^2} \int d\mathbf{k} \tilde{\mathbf{u}}(z, \mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{x} + \alpha t), \quad (15)$$

where, α is the growth rate, and \mathbf{x} and \mathbf{k} are the (two-dimensional) position vector and wave vector in the x - y plane, respectively. Since the gel is isotropic in the x - y plane, in the remainder of the section we assume that the wave vector is directed along the x axis without loss of generality. The eigenfunction in the z direction, $\tilde{\mathbf{u}}(z, \mathbf{k})$, is determined from single fluid conservation equations (12) and (13). To facilitate an asymptotic analysis in small ϵ , the growth rate and the perturbations to the displacement field are expressed as an expansion in ϵ :

$$\alpha = \alpha^{(0)} + \epsilon \alpha^{(1)}, \quad \tilde{\mathbf{u}} = \tilde{\mathbf{u}}^{(0)} + \epsilon \tilde{\mathbf{u}}^{(1)}. \quad (16)$$

In the leading order approximation we neglect the viscous dissipation term in the momentum conservation equation,

and the linearized mass and momentum conservation equations can be simplified to the following form:

$$D\tilde{u}_z^{(0)} + ik\tilde{u}_x^{(0)} = 0, \quad (17)$$

$$-D\tilde{p}^{(0)} + [-(\alpha^{(0)})^2 + D^2 - k^2]\tilde{u}_z^{(0)} = 0, \quad (18)$$

$$-ik\tilde{p}^{(0)} + [-(\alpha^{(0)})^2 + D^2 - k^2]\tilde{u}_x^{(0)} = 0. \quad (19)$$

Here, D represents the derivative ($\partial/\partial z$). The conservation equations for the $O(\epsilon)$ correction to the displacement field contain viscous terms:

$$D\tilde{u}_z^{(1)} + ik\tilde{u}_x^{(1)} = 0, \quad (20)$$

$$-D\tilde{p}^{(1)} + [-(\alpha^{(0)})^2 + D^2 - k^2]\tilde{u}_z^{(1)} + [-2\alpha^{(0)}\alpha^{(1)} + \alpha^{(0)}(D^2 - k^2)]\tilde{u}_z^{(0)} = 0, \quad (21)$$

$$-ik\tilde{p}^{(1)} + [-(\alpha^{(0)})^2 + D^2 - k^2]\tilde{u}_x^{(1)} + [-2\alpha^{(0)}\alpha^{(1)} + \alpha^{(0)}(D^2 - k^2)]\tilde{u}_x^{(0)} = 0. \quad (22)$$

The equations for the perturbations to the stresses in gel are

$$\tilde{\sigma}_{zz}^{(0)} = -\tilde{p}^{(0)} + 2D\tilde{u}_z^{(0)}, \quad \tilde{\sigma}_{xz}^{(0)} = D\tilde{u}_x^{(0)} + ik\tilde{u}_z^{(0)}, \quad (23)$$

$$\tilde{\sigma}_{zz}^{(1)} = -\tilde{p}^{(1)} + 2D\tilde{u}_z^{(1)} + 2\alpha^{(0)}D\tilde{u}_z^{(0)},$$

$$\tilde{\sigma}_{xz}^{(1)} = D\tilde{u}_x^{(1)} + ik\tilde{u}_z^{(1)} + \alpha^{(0)}(D\tilde{u}_x^{(0)} + ik\tilde{u}_z^{(0)}). \quad (24)$$

The $O(1)$ and $O(\epsilon)$ contributions to the zero stress boundary conditions (14) are

$$\text{At } z=h(x): \quad \tilde{\sigma}_{xz}^{(0)} = 0, \quad \tilde{\sigma}_{zz}^{(0)} = -\Gamma k^2 \tilde{u}_z^{(0)}, \quad (25)$$

$$\tilde{\sigma}_{xz}^{(1)} = 0, \quad \tilde{\sigma}_{zz}^{(1)} = -\Gamma k^2 \tilde{u}_z^{(1)}, \quad (26)$$

These are argued by the appropriate boundary conditions at $z=-H$, (10) or (11).

The eigenfunctions for the $O(1)$ and $O(\epsilon)$ mass and momentum equations can be expressed in the following compact form:

$$\begin{pmatrix} \tilde{u}_z^{(n)} \\ \tilde{u}_x^{(n)} \end{pmatrix} = A_{ij}^{(n)} \begin{pmatrix} \exp(kz) \\ \exp(\lambda z) \\ \exp(-kz) \\ \exp(-\lambda z) \end{pmatrix}, \quad (27)$$

where the decay rate of perturbations in the gel, λ , is

$$\lambda = \sqrt{k^2 + (\alpha^{(0)})^2}. \quad (28)$$

In (27), $n=0$ refers to the solutions of the leading order equations (17), (18), and (19), and $n=1$ refers to the solutions of the $O(\epsilon)$ equations (20), (21), and (22). $A_{ij}^{(0)}$ is a 2×4 matrix of complex amplitudes of the perturbations fields. This contains four independent coefficients, while the other four can be determined from the mass conservation condition (17). One of the four constants can be chosen arbitrarily, since only the relative amplitudes of the modes are relevant to the analysis. The dispersion relation for the leading order growth rate $\alpha^{(0)}$ is obtained after solving for the remaining three constants using the

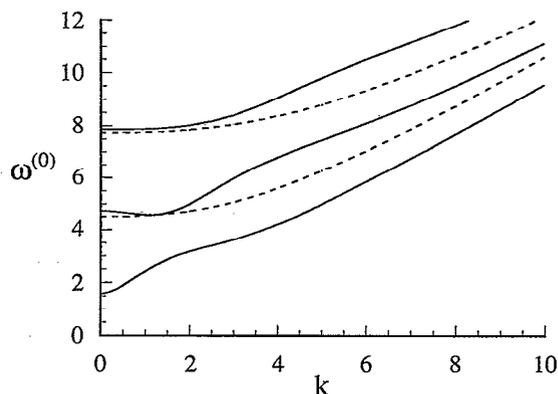


FIG. 3. Frequency spectrum of the first few harmonics for a grafted gel in the limit $\Gamma \rightarrow 0$ (solid lines) and $\Gamma \rightarrow \infty$ (broken lines).

zero stress conditions at $z=h(x)$, (25), and the appropriate conditions at $z=-H$, (10) or (11). The matrix of coefficients for the $O(\epsilon)$ correction to the displacement field $A_{ij}^{(1)}$ also contains four independent constants, and the dispersion relations for the first correction to the growth rate $\alpha^{(1)}$ is obtained by a procedure identical to that described above.

The dispersion relation is more complex than those for semi-infinite media, due to the nontrivial boundary conditions at $z=-H$, and we do not write it out in full detail here. However, it is useful to note that in the limit $H \rightarrow \infty$, our dispersion relation is identical to that obtained by Harden *et al.*,⁸ and this serves as a check on the accuracy of our calculations.

B. Results

We first note that the leading order growth rate $\alpha^{(0)}$ is purely imaginary, since there is no viscous dissipation in the leading order equations (17), (18), and (19). The imaginary part of $\alpha^{(0)}$ is termed the leading order frequency $\omega^{(0)}$. The dispersion relation admits many solutions for the frequency, corresponding to the different modes of oscillation of the gel. The characteristics of these modes for grafted and adsorbed gels are described below. The first correction to the growth rate $\alpha^{(1)}$ is real and negative, since the viscous dissipation of energy dampens the fluctuations in the system. Note that the leading order frequency $\omega^{(0)}$ is $O[E/(\rho H^2)]^{1/2}$, whereas decay rate of the perturbations, $(-\alpha^{(1)})$, is $O(E/\eta)$. Thus the decay of the perturbations occurs over time scales that are $O(1/\epsilon)$ larger than the time period of the elastic oscillations. We present results for the frequency and growth rate in two asymptotic limits, $\Gamma \rightarrow 0$ and $\Gamma \rightarrow \infty$, as well as the behavior of the lowest harmonic in the intermediate regime.

The frequencies of oscillation $\omega^{(0)}$ for a grafted gel [boundary condition (10)] have the following characteristics. In the limit $k \rightarrow 0$, the permitted frequencies are $\pi/2, 3\pi/2, 5\pi/2, \dots$. The first three harmonics are shown as the solid lines in Fig. 3. The lowest harmonic increases proportional to $0.95513k$ in the limit $k \rightarrow \infty$, while the higher harmonics converge to the solution $\omega^{(0)} = k$ in this limit.

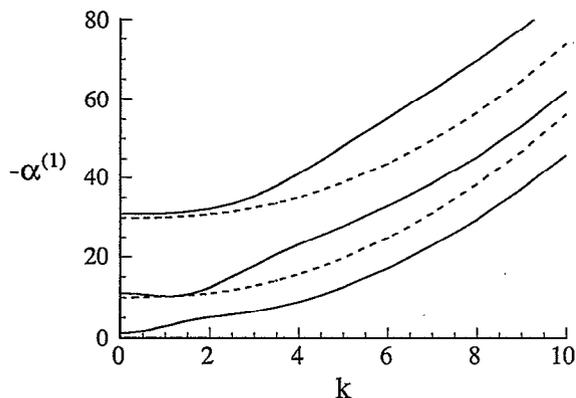


FIG. 4. Decay rate of the first few harmonics for a grafted gel in the limit $\Gamma \rightarrow 0$ (solid lines) and $\Gamma \rightarrow \infty$ (broken lines).

The solid lines in Fig. 4 show the decay rates, $(-\alpha^{(1)})$, of the first three harmonics. In the limit $k \rightarrow 0$, the decay rate $(-\alpha^{(1)})$ is proportional to $(\omega^{(0)})^2/2$. Thus the higher harmonics have much faster decay rates, and their persistence time is significantly shorter. In the limit $k \rightarrow \infty$, the decay rate of the lowest harmonic increases as $0.4563k^2$, whereas the decay rates of the higher harmonics increase as $0.5k^2$.

In the limit $\Gamma \rightarrow \infty$, we once again have multiple solutions for the frequency. The frequencies $\omega^{(0)}$ of the first two harmonics, which are shown as broken lines in Fig. 3, assume values of 4.493 and 7.725 in the limit $k \rightarrow 0$, and converge to $k[1 - (n\pi/k)^2]$ in the limit $k \rightarrow \infty$. Here, n is an integer that denotes the order of the harmonic, and is 1 for the lowest harmonic. The decay rates of these harmonics are shown as broken lines in Fig. 4. These increase as $(\omega^{(0)})^2/2$ for $k \rightarrow 0$, and converge to $0.5k^2$ for $k \rightarrow \infty$.

The frequency and decay rates of the lowest harmonic for intermediate values of Γ are shown in Figs. 5 and 6. In the limit $k \rightarrow 0$, all the solutions converge to the $\Gamma \rightarrow 0$ solution, whereas in the limit $k \rightarrow \infty$ the solutions for different values of Γ collapse onto the $\Gamma \rightarrow \infty$ curve. We note that even for Γ as large as 100, the frequency and decay rates diverge significantly from the $\Gamma \rightarrow \infty$ solution for

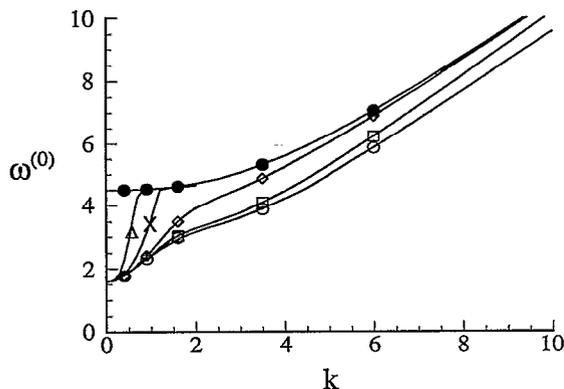


FIG. 5. Frequency spectrum of the lowest harmonic for a grafted gel in the intermediate Γ regime. $\circ - \Gamma = 0.0$; $\square - \Gamma = 0.1$; $\diamond - \Gamma = 1.0$; $\times - \Gamma = 10.0$; $\triangle - \Gamma = 100.0$; $\bullet - \Gamma = \infty$.

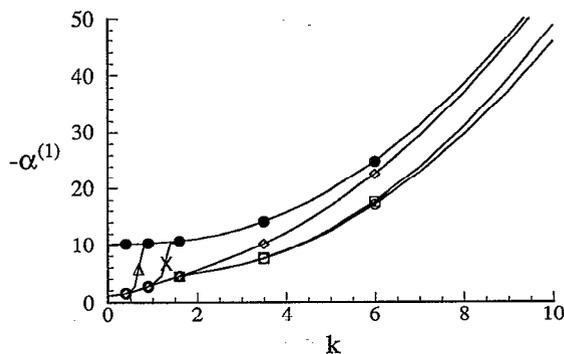


FIG. 6. Decay rate of the lowest harmonic for a grafted gel in the intermediate Γ regime. $\circ - \Gamma = 0.0$; $\square - \Gamma = 0.1$; $\diamond - \Gamma = 1.0$; $\times - \Gamma = 10.0$; $\triangle - \Gamma = 100.0$; $\bullet - \Gamma = \infty$.

$k < 1$, whereas for $\Gamma = 0.01$, the frequency does not show significant deviation from the $\Gamma = 0$ solution even for k as large as 10. Thus the solution in the limit $\Gamma = 0$ is more robust, and could be used for moderately small values of Γ , whereas the solution for $\Gamma \rightarrow \infty$ will not be valid for moderately large values of Γ if k is small.

The solutions for the frequency and decay rate for an adsorbed gel [boundary condition (11)] for $\Gamma \rightarrow 0$ are shown as the solid lines in Figs. 7 and 8. The frequency $\omega^{(0)}$ assumes values $0, \pi, 2\pi, \dots$ in the limit $k \rightarrow 0$, and the decay rate, $(-\alpha^{(1)})$, is proportional to $(\omega^{(0)})^2/2$. The broken lines in Figs. 7 and 8 show the frequency and decay rate for $\Gamma \rightarrow \infty$. The frequency $\omega^{(0)}$ assumes values of $\pi, 2\pi, \dots$, for $k \rightarrow 0$, and the decay rate $(-\alpha^{(1)})$ is proportional to $(\omega^{(0)})^2/2$ as before. In the limit $k \rightarrow \infty$, the length scale of the perturbations is much smaller than the gel thickness and the choice of boundary conditions at $z = -H$ does not affect the solution. Therefore, the behavior of the frequency and decay rate for $k \rightarrow \infty$ is the same as that for a grafted gel. The frequency and decay rate of the lowest harmonic for intermediate values of Γ , which are shown in Figs 9 and 10, have the same qualitative features as those for a grafted gel. The asymptotic behavior of the frequency and

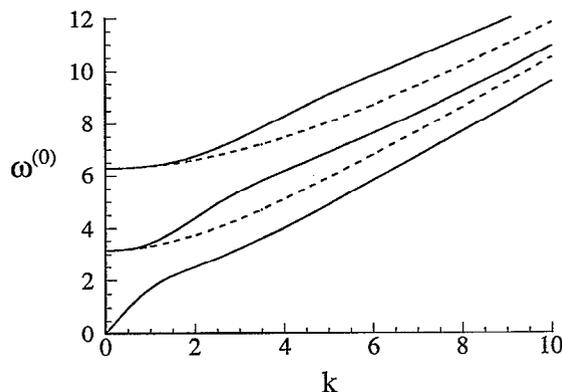


FIG. 7. Frequency spectrum of the first few harmonics for an adsorbed gel in the limit $\Gamma \rightarrow 0$ (solid lines) and $\Gamma \rightarrow \infty$ (broken lines).

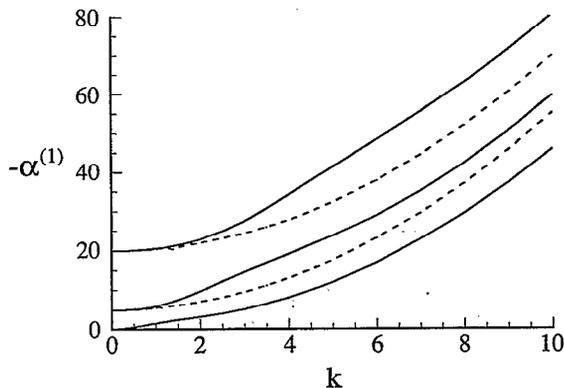


FIG. 8. Decay rate of the first few harmonics for an adsorbed gel in the limit $\Gamma \rightarrow 0$ (solid lines) and $\Gamma \rightarrow \infty$ (broken lines).

decay rate are listed in Table I for a grafted gel, and in Table II for an adsorbed gel.

Finally, we compare these results with those of Harden, Pleiner, and Pincus⁸ for a semi-infinite gel. In the elastic limit $\Gamma \rightarrow 0$, we recover the lowest harmonic in the limit $k \rightarrow \infty$ by solving the dispersion relation derived by Harden *et al.* However, in the capillary regime, which corresponds to the limit $\Gamma \rightarrow \infty$, the authors found that the frequency increases as $k^{3/2}$, which is very different from the $\omega^{(0)} \sim k$ behavior predicted by our analysis. This difference can be explained as follows. For a semi-infinite gel, the relevant length and time scales are (γ/E) and $[E^3/(\rho\gamma^2)]^{1/2}$, respectively. A simple dimensional analysis indicates that the dimensional frequency increases proportional to $k^{3/2}(\gamma/\rho)^{1/2}$. Also, for a semi-infinite gel, the boundary conditions imposed are zero displacement conditions for $z \rightarrow -\infty$, and purely imaginary values of the spatial decay rate of perturbations, [λ in (27) and (28)] are not permitted. If we impose zero displacement conditions at a fixed distance H , however, imaginary values of λ are permitted, and the equations admit solutions for the dimensional frequency that increase as $k(E/\rho)^{1/2}$. The ratio of the permitted frequencies for a semi-infinite and finite

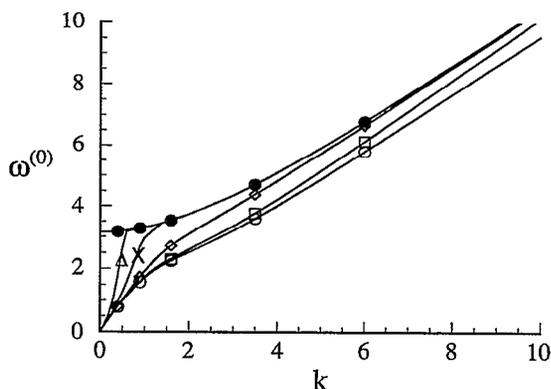


FIG. 9. Frequency spectrum of the lowest harmonic for an adsorbed gel in the intermediate Γ regime. \circ — $\Gamma=0.0$; \square — $\Gamma=0.1$; \diamond — $\Gamma=1.0$; \times — $\Gamma=10.0$; \triangle — $\Gamma=100.0$; \bullet — $\Gamma=\infty$.

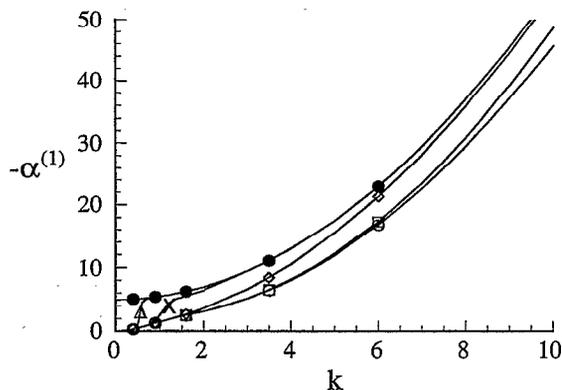


FIG. 10. Decay rate of the lowest harmonic for an adsorbed gel in the intermediate Γ regime. \circ — $\Gamma=0.0$; \square — $\Gamma=0.1$; \diamond — $\Gamma=1.0$; \times — $\Gamma=10.0$; \triangle — $\Gamma=100.0$; \bullet — $\Gamma=\infty$.

gel is $(\Gamma kH)^{1/2}$, which is always large for $\Gamma \gg 1$ and $kH \gg 1$. Thus in the large k limit the frequency and decay rate permitted by the dispersion relation for a finite gel are small compared to those for a semi-infinite gel. Consequently, the modes with the longest persistence times are those obtained from the finite gel dispersion relations.

IV. STRUCTURE FACTOR

The structure factor for a semi-infinite gel was calculated from a Langevin equation for the velocity field in the gel by Harden *et al.*⁸ This equation included a random stress tensor, whose autocorrelation is proportional to the viscosity of the gel. It turns out that this procedure is not appropriate for calculating the structure factor for our system for the following reason— if we neglect the viscosity of the gel at leading order in small ϵ , the autocorrelation of the random stress tensor is zero at this level of approximation, and consequently the structure factor obtained by this procedure is identically zero. Here, we use an alternate procedure for calculating the static and dynamic structure factors. The energy storage in the displacement field is expressed as a quadratic function of the amplitude of the surface displacement, and the static structure factor is read off from this relation. The dynamic structure factor is eas-

TABLE I. Asymptotic behavior of the frequency $\omega^{(0)}$ and decay rate $-\alpha^{(1)}$ of a grafted gel.

Regime	$\omega^{(0)}$	$-\alpha^{(1)}$
$\Gamma \rightarrow 0$	$\pi/2$	$(\omega^{(0)})^2/2$
$k \rightarrow 0$	$3\pi/2, 5\pi/2, \dots$	
$\Gamma \rightarrow 0$	$0.955313k$	$0.4563k^2$
$k \rightarrow \infty$	k	$0.5k^2$
$\Gamma \rightarrow \infty$	$4.493, 7.725, \dots$	$(\omega^{(0)})^2/2$
$k \rightarrow 0$		
$\Gamma \rightarrow \infty$	$k[1 - (1/2)(n\pi/k)^2]$	$0.5k^2$
$k \rightarrow \infty$		

TABLE II. Asymptotic behavior of the frequency $\omega^{(0)}$ and decay rate $-\alpha^{(1)}$ of an adsorbed gel.

Regime	$\omega^{(0)}$	$-\alpha^{(1)}$
$\Gamma \rightarrow 0$ $k \rightarrow 0$	0 $\pi, 2\pi, \dots$	$(\omega^{(0)})^2/2$
$\Gamma \rightarrow 0$ $k \rightarrow \infty$	$0.955313k$ k	$0.4563k^2$ $0.5k^2$
$\Gamma \rightarrow \infty$ $k \rightarrow 0$	$\pi, 2\pi, \dots$	$(\omega^{(0)})^2/2$
$\Gamma \rightarrow \infty$ $k \rightarrow \infty$	$k[1 - (1/2)(n\pi/k)^2]$	$0.5k^2$

ily calculated since the perturbations decay as a single exponential with a characteristic frequency and decay rate.

It is convenient to define the Fourier transforms of the displacement fields as follows:

$$\mathbf{u}(z, \mathbf{k}, \omega) = \int_{-\infty}^{\infty} dt \int d\mathbf{x} \exp(-i\mathbf{k} \cdot \mathbf{x} + i\omega t) \mathbf{u}(z, \mathbf{x}, t), \quad (29)$$

where \mathbf{x} and \mathbf{k} are the (two-dimensional) position vector and wave vector in the x - y plane. It can be easily verified that $\mathbf{u}(z, \mathbf{k}, t)$ and $\mathbf{u}(z, \mathbf{k}, \omega)$ are related to the displacement field, $\tilde{\mathbf{u}}(z, \mathbf{k})$ in Sec. III as follows:

$$\begin{aligned} \mathbf{u}(z, \mathbf{k}, t) &= \tilde{\mathbf{u}}(z, \mathbf{k}) \exp(\alpha t), \\ \mathbf{u}(z, \mathbf{k}, \omega) &= 2\alpha \tilde{\mathbf{u}}(z, \mathbf{k}) / (\omega^2 + \alpha^2). \end{aligned} \quad (30)$$

The static structure factor for the surface height $S(\mathbf{k})$ is defined as the equal time correlation function for the height of the surface $h(\mathbf{k})$:

$$S(\mathbf{k}) = \langle h(\mathbf{k}, t) h^*(\mathbf{k}, t) \rangle = \langle u_z(z, \mathbf{k}, t) u_z^*(z, \mathbf{k}, t) \rangle |_{z=0}. \quad (31)$$

The above definition is similar to the definition of the static structure factor in a fluid as the equal time density correlation function.¹³ In the second equality in the above expression, we approximate that the surface height by the displacement at $z=0$, which is permissible for small perturbations. Since the static structure factor is an equal time correlation function, we can replace $\mathbf{u}(z, \mathbf{k}, t)$ in the above equation by $\tilde{\mathbf{u}}(z, \mathbf{k})$ while calculating the averages.

The static structure factor is calculated from the change in the free energy of the gel due to an externally imposed displacement field. The free energy F is related to the displacement field as follows:

$$\begin{aligned} F &= \frac{EH^3}{T} \left[\int d\mathbf{x} \int_{-1}^0 dz \left(\frac{1}{4} \left| \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right|^2 + \frac{1}{2} \left| \frac{\partial u_i}{\partial t} \right|^2 \right) \right. \\ &\quad \left. + \Gamma \int d\mathbf{x} \frac{1}{2} \left| \frac{\partial h(\mathbf{x})}{\partial x_i} \right|^2 \right], \end{aligned} \quad (32)$$

where T is the product of the temperature and the Boltzmann constant, there is a factor of (E/T) on the left side of the above expression because free energy is expressed in units of T , and a factor of H^3 because the length scales are nondimensionalized by H . The first integral on the right

side contains the standard expression for the elastic energy due to the strain in the gel¹¹ and the kinetic energy. The second integral is the change in the free energy due to the deformation of the surface.¹⁰ To derive the structure factor, it proves convenient to express the free energy in terms of the Fourier components of the displacement field using (30). After some algebraic manipulations, which include expressing \tilde{u}_x in terms of \tilde{u}_z using (17), we get

$$\begin{aligned} F &= \frac{EH^3}{8\pi^2 T} \left(\int_{-1}^0 dz \int d\mathbf{k} k^{-2} \{ (D^2 + k^2) \tilde{u}_z (D^2 + k^2) \tilde{u}_z^* \right. \\ &\quad \left. + 4k^2 D \tilde{u}_z D \tilde{u}_z^* + \alpha \alpha^* [k^2 \tilde{u}_z \tilde{u}_z^* + (D \tilde{u}_z) (D \tilde{u}_z^*)] \} \right. \\ &\quad \left. + \Gamma \int d\mathbf{k} k^2 \tilde{h} \tilde{h}^* \right), \end{aligned} \quad (33)$$

where the variables with superscript * are the complex conjugates of the variables without the superscript, and \tilde{h} is the Fourier transform of the displacement \tilde{u}_z at $z=0$.

The structure factor for the surface modes can be related to the free energy of the fluctuations using the fluctuation dissipation theorem in the linear regime. The change in the height of the interface $h(\mathbf{x})$ due to an applied potential $\mu(\mathbf{x})$ which is conjugate to the surface height, is given by

$$h(\mathbf{x}) = \int d\mathbf{x}' \chi(\mathbf{x} - \mathbf{x}') \mu(\mathbf{x}'), \quad \tilde{h}(\mathbf{k}) = \chi(\mathbf{k}) \mu(\mathbf{k}), \quad (34)$$

where the response function $\chi(\mathbf{k})$ is related to the structure factor $S(\mathbf{k})$ via the fluctuation-dissipation theorem:²

$$\chi(\mathbf{k}) = TS(\mathbf{k}). \quad (35)$$

The increase in the energy due to a small perturbation about the equilibrium state is equal to the product of the change in the surface height and the conjugate potential, and it is easy to see that the leading order contribution to the energy is quadratic in the surface height. In real space, the change in the energy can be expressed as

$$F = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \chi(\mathbf{x} - \mathbf{x}')^{-1} h(\mathbf{x}) h(\mathbf{x}'). \quad (36)$$

Expressing the height $h(\mathbf{x})$ and the response function $\chi(\mathbf{x})$ in terms of the Fourier components $\tilde{h}(\mathbf{k})$ and $\chi(\mathbf{k})$, and using (35) to relate the response function to the structure factor, we end up with the standard expression for the change in the free energy F of the gel due to a small change in the variable $h(\mathbf{k})$ about equilibrium:

$$F = \frac{1}{8\pi^2} \int d\mathbf{k} S(\mathbf{k})^{-1} \tilde{h}(\mathbf{k}) \tilde{h}^*(\mathbf{k}), \quad (37)$$

where F is nondimensionalized by T . Note that the change in the free energy in (33) has the same form as that in (37) once the integral over the z coordinate is carried out. Therefore, our method of solution involves carrying out the integral over the z coordinate in (33) and expressing the resulting equation in terms of the displacement $\tilde{h}(\mathbf{k})$. Once this is done, the structure factor is just equal to the inverse of the prefactor in the resulting expression.

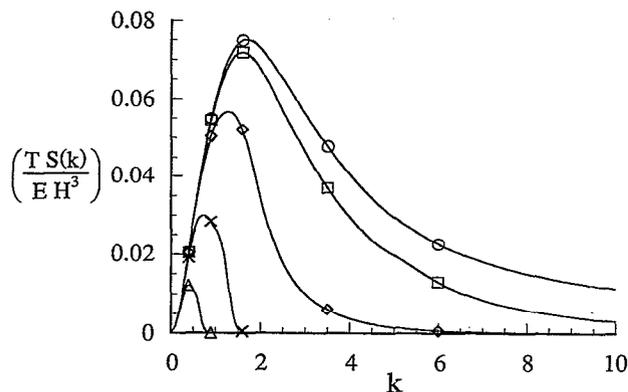


FIG. 11. The scaled structure factor $[S(k)T/(EH^3)]$, for the lowest harmonic of the surface modes on a grafted gel. $\circ - \Gamma=0.0$; $\square - \Gamma=0.1$; $\diamond - \Gamma=1.0$; $\times - \Gamma=10.0$; $\triangle - \Gamma=100.0$.

The dynamic structure factor $S(\mathbf{k}, \omega)$ is the temporal Fourier transform of the memory function $G(\mathbf{k}, t)$ which is defined as

$$G(\mathbf{k}, t) = \langle h(\mathbf{k}, t) h^*(\mathbf{k}, 0) \rangle = \langle u_z(z, \mathbf{k}, t) u_z^*(z, \mathbf{k}, 0) \rangle \Big|_{z=0}. \quad (38)$$

The static structure factor and memory function are related to the rate of dissipation of energy via the fluctuation dissipation theorem. However, in the linear regime, the perturbations decay exponentially and the memory function is easily expressed in terms of the static structure factor:

$$G(\mathbf{k}, t) = S(\mathbf{k}) \exp(-\alpha |t|). \quad (39)$$

The dynamic structure factor is calculated by taking the temporal Fourier transform of the above expression:

$$S(\mathbf{k}, \omega) = 2\alpha S(\mathbf{k}) / (\omega^2 + \alpha^2), \quad (40)$$

where α is $(i\omega^{(0)} + \alpha^{(1)})$, and $\omega^{(0)}$ and $\alpha^{(1)}$ are shown in Figs. 2–10. If we neglect viscous dissipation, the dynamic structure factor is a delta function at the vibrational frequency $\omega^{(0)}$. The decay rate $-\alpha^{(1)}$ causes a small spread in the dynamic structure factor.

In this section, we present calculations of the static structure factor of the lowest harmonic, which has the lowest frequency of oscillation, for grafted and adsorbed gels. The kinetic energy and the strain energy penalty for this harmonic are smaller than those for the higher harmonics, and consequently this has the largest amplitude of surface fluctuations. Also, the decay rate of this harmonic is smaller than those for the higher harmonics, and so this is likely to be the easiest to observe in experiments. The static structure factor $S(\mathbf{k})$ is proportional to (EH^3/T) [see (33)], and Fig. 11 shows the scaled structure factor $[S(\mathbf{k})T/(EH^3)]$ for the lowest harmonic of a *grafted gel* [boundary condition (10)]. The structure factor increases proportional to k^2 in the limit $k \rightarrow 0$, and rises to a maximum before decreasing to zero for large k . The decrease in the structure factor for large k is due to the excessive energy required for maintaining perturbations of small wave-

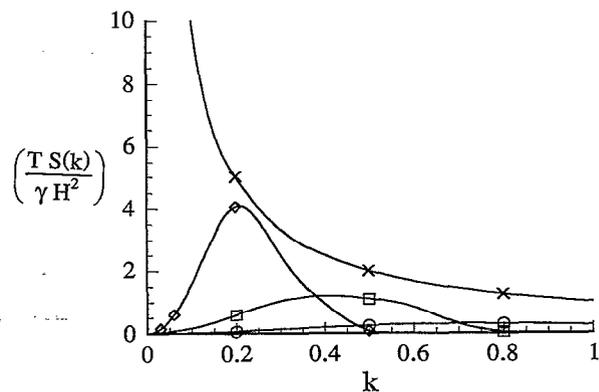


FIG. 12. The scaled structure factor $[S(k)T/(\gamma H^2)]$, for the lowest harmonic of the surface modes on a grafted gel. $\circ - \Gamma=1.0$; $\square - \Gamma=10.0$; $\diamond - \Gamma=100.0$; $\times - \Gamma=\infty$.

length, while the small k behavior can be explained as follows. The boundary conditions (10) do not permit lateral displacement at $z = -H$, and therefore perturbations having amplitudes h and wavelengths $k \ll 1$ induce displacements of $O(h/k)$ in the x direction [see (17)]. Thus the lateral strain due to these perturbations $(\partial u_x / \partial z)$ is $O(h/k)$, and the elastic strain energy is $O(h/k)^2$, giving the $O(k)^2$ behavior of the structure factor for small k . Both the position and the height of the peak decrease as Γ is increased, since an increase in the surface tension preferentially damps out smaller wavelength (larger k) fluctuations.

The structure factor has an interesting behavior in the limit of large Γ . In this limit, the interfacial energy is large compared to the elastic strain energy, and it is appropriate to define the scaled structure factor as $[S(\mathbf{k})T/(\gamma H^2)]$. If the elastic energy is neglected in the limit $\Gamma = \infty$, it can be easily seen from (33) that $[S(\mathbf{k})T/(\gamma H^2)]$ is just k^{-2} . This structure factor is divergent in the limit $k \rightarrow 0$ because the excess surface area decreases proportional to k^2 for long wavelength fluctuations, and consequently the energy penalty also decreases to zero. If Γ is large but finite, however, the elastic energy cost becomes significant for small k , and the structure factor decreases to zero at small values of k as shown in Fig. 12. Thus the long wavelength behavior of the structure factor for large Γ deviates significantly from the asymptotic behavior in the limit $\Gamma \rightarrow \infty$. We also note in passing that the singularity in the structure factor at small k for $\Gamma \rightarrow \infty$ would be modified by the effect of gravity, and we would expect, based on scaling considerations, that the effect of gravity is significant for $(kH) \sim (\rho g H^2 / \gamma)^{1/2}$. The dimensionless quantity $(\rho g H^2 / \gamma)^{1/2}$ varies between 0.7 at $H = 1$ mm, 0.7×10^{-3} for $H = 1$ μ m for $\rho = 10^3$ kg/m³ and $\gamma = 20 \times 10^{-3}$ N/m.

The scaled structure factor for the lowest harmonic of an *adsorbed gel* [boundary condition (11)], shown in Fig. 13, is qualitatively very different from that for a grafted gel. The structure factor has a finite value at $k=0$, and decreases as we increase k . The nonzero value of the structure factor at $k=0$ is rather surprising in view of the sole-

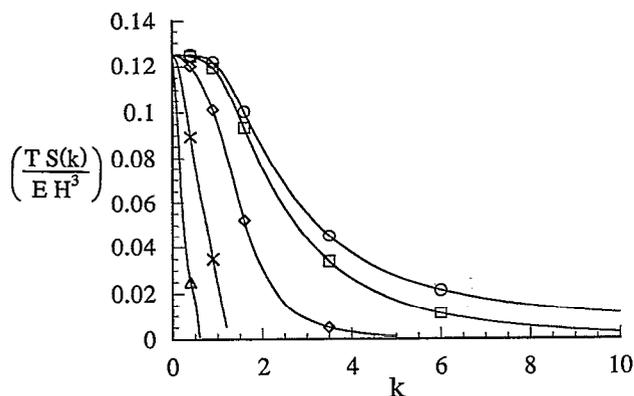


FIG. 13. The scaled structure factor $[S(k)T/(EH^3)]$, for the lowest harmonic of the surface modes on an adsorbed gel. $\circ - \Gamma=0.0$; $\square - \Gamma=0.1$; $\diamond - \Gamma=1.0$; $\times - \Gamma=10.0$; $\triangle - \Gamma=100.0$.

noidal condition (17) imposed on the displacement field, and the reason for this is the unconstrained lateral displacement at $z=-H$. As in the case of a fixed gel, a perturbation with wave number $k \ll 1$ and amplitude h induces a lateral displacement u_x that is $O(h/k)$. However, due to the zero shear stress boundary condition at $z=-H$, the lateral strain rate $(\partial u_x/\partial z)$ is only $O(h)$, and is $O(k)$ smaller than the strain we would expect from a naive scaling argument. Therefore, the energy required to produce the strain is $O(h^2)$ in the limit $k \rightarrow 0$ and the structure factor assumes a finite value in this limit. Also, the elastic energy required for maintaining the perturbations in an adsorbed gel is smaller than that for a grafted gel, due to the zero shear stress condition at $z=-H$. Therefore, the magnitude of the structure factor is larger for the adsorbed gel. We should also note that our analysis has neglected boundaries in the x - y plane. These boundaries would be present in any experimental system, and would limit the permissible wavelengths of the fluctuations.

V. DISCUSSION

In this paper, we analyzed the surface modes on the gel in the limit where the ratio of the elastic oscillation time and viscous relaxation time $\epsilon = [\eta^2/(\rho EH^2)]^{1/2}$ is small, using an asymptotic approach in the limit $\epsilon \ll 1$. A scaling analysis in Sec. II showed that this assumption is valid when the thickness of the gel is large compared to $1 \mu\text{m}$ for normal values of the gel elasticity and viscosity. In this limit, there is a balance between the elastic and surface tension forces at leading order, while the viscous dissipation enters as an $O(\epsilon)$ correction in the equations of motion. Since there are no dissipative forces in the leading order equations, the leading order decay rate of the fluctuations is purely imaginary, indicating that the surface modes propagate undamped over time scales comparable to the elastic oscillation time. The viscous damping takes place over time scales comparable to the viscous relaxation time, which is $O(1/\epsilon)$ larger than the elastic time.

The dynamics of the gel was analyzed using coupled equations for the polymer network and the fluid (two-fluid

model), and we made the “infinite coupling approximation,” which sets the local velocity of the network equal to that of the fluid. This approximation is valid when the mesh size of the gel, which is usually 100 \AA or less, is small compared to the length scales of interest in the problem. Zero stress boundary conditions were applied at the free surface of the gel [$z=h(x)$], while two different types of boundary conditions were studied at the other bounding surface at $z=-H$; for “grafted gels” zero displacement conditions were applied at this surface; while for “adsorbed gels” the surface was bounded in the normal direction, but was free to move in the tangential direction, and the shear stress was set equal to zero at this surface.

For both grafted and adsorbed gels, we observe the presence of multiple frequencies for the surface oscillations, all of which are consistent with the boundary conditions at $z=-H$. In the limit of large wave number ($k \gg 1$), the frequencies of the surface oscillations increase proportional to k and the decay rates of the perturbations increase proportional to k^2 . The frequencies and decay rates are finite in the limit $k \rightarrow 0$, and their value depends on the boundary conditions applied at $z=-H$; these are summarized in Tables I and II. The frequencies of oscillation and the decay rates are lower for adsorbed gels than for grafted gels, and an increase in the surface tension increases the frequency and the decay rates of the perturbations in the limit $k \rightarrow 0$. We also note that in the surface tension dominated regime, the frequency increases proportional to the wave number k in the limit $k \rightarrow \infty$, which is different from the $k^{3/2}$ dependence semi-infinite gels. This qualitative difference can be explained as follows— only modes that decay exponentially in the direction normal to the surface are permissible for semi-infinite gels, whereas solutions that have an oscillatory behavior in this direction are allowed for finite gels. The frequency and decay rate of the exponentially decaying solution for semi-infinite gels increases proportional to $k^{3/2}$ and k^3 , respectively, in the surface tension dominated regime, whereas the frequency and decay rate of the oscillating solutions permitted for finite gels have a much slower increase proportional to k and k^2 for large k . Hence, for finite gels we obtain certain solutions that cannot be recovered from an analysis of semi-infinite gels in the surface tension dominated regime, and these solutions may be important from an experimental point of view because they have much lower decay rates than the modes for semi-infinite gels.

The structure factor for the lowest harmonic of the surface modes was calculated from the energy storage in the elastic strain field, the surface deformation, and the kinetic energy of the gel. A simple dimensional analysis indicates that the magnitude of the surface factor is proportional to (EH^3/T) . For a *grafted gel*, the structure factor decreases proportional to k^2 for $k \rightarrow 0$, because the strain in the x direction due to a surface displacement h is proportional to (h/k) , and the elastic energy required to maintain the strain field increases proportional to $(h/k)^2$. The structure factor has a peak at a finite value of k , and then decreases at large k because of the large energy required to sustain small wavelength perturbations.

The structure factor for the lowest harmonic of an *adsorbed gel* is very different from that for a grafted gel. The strain in the x direction due to a surface displacement of magnitude h , is $O(h)$, because the surface is not constrained in the x direction at $z = -H$. This is $O(k)$ smaller than the strain we would expect from a naive scaling argument. Due to this, the elastic energy in the strain field is finite for $k \rightarrow 0$, and the structure factor has a peak at this value. We also note that the magnitude of the structure factor for an adsorbed gel is greater than that for a grafted gel, because the adsorbed gel is unconstrained in the x direction at $z = -H$, and the strain energy required for a displacement h is smaller than that required for an equal displacement in a grafted gel.

An increase in the surface tension decreases the maximum value of the structure factor due to the higher energy required to produce perturbations of the same magnitude. The surface tension also preferentially dampens the large wave number perturbations, and shifts the peak in the structure factor to lower wave numbers. Our analysis shows that even at large values of the parameter Γ , the elastic effects are important for small wave numbers, since the elastic energy becomes greater than the surface energy in the limit $k \rightarrow 0$.

The above analysis indicates that there are significant qualitative differences between the modes for a semi-infinite and a finite gel in the surface tension dominated regime. The dynamics of the gel is also sensitive to the boundary conditions applied at the other bounding surface of the gel, and the structure factor for an adsorbed gel is qualitatively different from that for a grafted gel. This difference should be observable in experiments. The above analysis also provides us with some understanding about the surface modes on finite gels with two free surfaces. In Sec. II we showed that the boundary conditions for grafted

and adsorbed gels are identical to those at the midplane of a gel with two free surfaces having antisymmetric [Fig. 2(a)] and symmetric [Fig. 2(b)] perturbations, respectively. Since the structure factor for an adsorbed gel is larger in magnitude than that for a grafted gel, the symmetric perturbations are likely to be larger in magnitude than the antisymmetric ones in a gel with two free surfaces.

ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The author had instructive discussions with Professor G. H. Fredrickson, Professor P. Pincus, and Dr. J. L. Harden.

- ¹A. Silberberg, *Physico Chem. Hydrodynam.* **9**, 419 (1987).
- ²P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell U. P., Ithaca, NY 1979).
- ³M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford U. P., New York, 1986).
- ⁴M. Sano, M. Kawaguchi, Y.-L. Chen, R. J. Skarupka, T. Chang, G. Zagari, and H. Yu, *Rev. Sci. Instrum.* **57**, 1158 (1986).
- ⁵H. Pleiner, J. L. Harden, and P. A. Pincus, *Europhys. Lett.* **7**, 383 (1988).
- ⁶E. S. G. Shaqfeh, R. G. Larson, and G. H. Fredrickson, *J. Non-Newtonian Fluid Mech.* **31**, 87 (1989).
- ⁷K. P. Chen, *J. Non-Newtonian Fluid Mech.* **40**, 155 (1991).
- ⁸J. L. Harden, H. Pleiner, and P. A. Pincus, *J. Chem. Phys.* **94**, 5208 (1991).
- ⁹V. Kumaran, G. H. Fredrickson, and P. A. Pincus, submitted *Phys. Fluids*.
- ¹⁰L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1989).
- ¹¹L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1989), Chap. 1.
- ¹²P.-G. de Gennes, *Macromolecules*, **9**, 594 (1976).
- ¹³B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Kreiger, Malabar, FL, 1990), Chap. 10.